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VIII.

CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF HARVARD COLLEGE.

RESEARCHES ON THE SUBSTITUTED BENZYL COMPOUNDS.

TWELFTH PAPER.

CERTAIN PARABROMBENZYL COMPOUNDS.

By C. Loring Jackson and G. T. Hartshorn.

Presented April 11th, 1883.

In a previous paper of this series a number of parachlorbenzyl compounds containing sulphur were described; in the following paper we have the honor of laying before the Academy a description of the corresponding compounds made from the parabrombenzylbromide.*

Parabrombenzylsulpho-acid, $C_6H_4BrCH_2SO_3H$.

The potassium salt of this substance was made by heating parabrombenzylbromide with an aqueous solution of neutral potassic sulphite in a flask with a return-cooler until the odor of the bromide disappeared. It was purified by crystallization from water, and dried first *in vacuo*, and afterwards at 110°, which showed that it contained no water of crystallization.

0.2230 g. of the substance gave, according to Carius, 0.1454 g. of argentic bromide.

0.2624 g. gave 0.1724 g. of argentic bromide, and 0.2140 g. of baric sulphate.

0.2224 g., after evaporation with sulphuric acid, gave 0.0688 g. of potassic sulphate.

	Calculated for $C_7H_6BrSO_3K$.	Found.	
Bromine	27.67	27.75	27.96
Sulphur	11.07		11.20
Potassium	13.50	13.89	

* The results obtained will be found in tabular form at the end of the article.

It crystallizes in narrow plates, which not infrequently reach a length of over one centimeter, and are characterized by a well-marked cleavage at right angles to their longer axis. On one occasion rhombic forms similar to those of the sodium salt of the parachlorbenzylsulpho-acid were observed. It is not freely soluble in cold water or alcohol, but its solubility in each of these solvents is much increased by heat. The solubility in water at 18° was determined as follows: —

I. 3.2760 g. of the saturated solution gave 0.2016 g. of the salt.

II. 2.7104 g. gave 0.1689 g. of the salt.

Percentage of $C_6H_4BrCH_2SO_3K$ in aqueous solution saturated at 18°: —

I.	II.
6.15	6.25

To make the other salts of the sulpho-acid, the crude potassium salt was treated with a small quantity of plumbic acetate, to free it from bromide and sulphite; and, after filtering from the precipitate thus formed, the lead salt was thrown down by adding an excess of plumbic acetate, and purified by crystallization from water. It was then suspended in water, and treated with sulphuretted hydrogen to convert it into the free acid, which was used in the preparation of the following salts.

The *Calcium Salt* $(C_6H_4BrCH_2SO_3)_2Ca$, made by warming the acid with calcic carbonate, and purified by crystallization from water, was free from water of crystallization.

0.4472 g. of the salt dried at 110° gave 0.1096 g. of calcic sulphate.

0.2870 g. gave 0.0715 g. of calcic sulphate.

	Calculated for $(C_7H_6BrSO_3)_2Ca$.	Found.	
Calcium	7.41	7.21	7.33

The salt crystallizes in long colorless plates, and is freely soluble in water.

The *Barium Salt* $(C_6H_4BrCH_2SO_3)_2BaH_2O$ was made from the acid with baric carbonate, and purified by crystallization from water.

0.4300 g. of the salt dried *in vacuo* lost, when heated to 110°, 0.0124 g. of water.

0.4396 g. lost 0.0123 g. of water.

	Calculated for $(C_7H_6BrSO_3)_2BaH_2O$.	Found.	
Water	2.75	2.88	2.80

0.1630 g. of dried salt gave 0.0592 g. of baric sulphate.

0.3625 g. gave 0.1314 g. of baric sulphate.

	Calculated for $(C_7H_6BrSO_3)_2Ba$.	Found.	
Barium	21.50	21.35	21.31

It crystallizes in stellate groups of white needles, and is slightly deliquescent. Its solubility in water was determined as follows: —

I. 4.0670 g. of the solution saturated at 18° gave 0.1649 g. of the salt.

II. 4.1510 g. gave 0.1679 g. of the salt.

Percentage of $(C_6H_4BrCH_2SO_3)_2Ba$ in aqueous solution saturated at 18°: —

I.	II.
40.55	40.46

The *Lead Salt* $(C_6H_4BrCH_2SO_3)_2Pb$, made and purified as already described, was free from water of crystallization.

0.3144 g. of the salt dried at 110° gave on combustion 0.2709 g. of carbonic dioxide, and 0.0481 g. of water.

0.2988 g. of the salt gave 0.1297 g. of plumbic sulphate.

	Calculated for $(C_7H_6BrSO_3)_2Pb$.	Found.
Carbon	23.76	23.51
Hydrogen	1.69	1.70
Lead	29.28	29.66

It crystallizes in radiating groups of long white needles. Its solubility in water was determined as follows: —

I. 4.3370 g. of the solution saturated at 18° gave 0.0873 g. of the salt.

II. 3.4536 g. gave 0.0691 g. of the salt.

Percentage of $(C_6H_4BrCH_2SO_3)_2Pb$ in aqueous solution saturated at 18°: —

I.	II.
2.01	2.00

The *Chloride* of the *Sulpho-acid* $C_6H_4BrCH_2SO_2Cl$ was made by grinding the dry potassium salt in a mortar with phosphoric pentachloride, and finishing the reaction by a gentle heat. The substance was precipitated on the addition of water as an oil, which solidified on

standing, and was purified by crystallization from ether or ligroine. It was dried *in vacuo* and analyzed.

0.2460 g. of substance gave, by the method of Carius, 0.3000 g. of the mixture of argentic chloride and argentic bromide, and 0.2028 g. of baric sulphate.

	Calculated for $C_7H_6BrSO_2Cl$.	Found.
Chlorine and Bromine	42.85	42.50
Sulphur	11.87	11.35

It crystallizes in small white prisms with a peculiar smell, similar to that of parabrombenzylbromide; but when cold it does not attack the mucous membrane, and when warmed only in a very much less degree than any of the brombenzylbromides. It melts at 115°, is essentially insoluble in water, and but slightly soluble in cold alcohol, ligroine, carbonic disulphide, and glacial acetic acid, freely soluble in all these solvents when hot, and in benzol and ether even in the cold.

Parabrombenzylsulphide, $(C_6H_4BrCH_2)_2S$.

This substance was made by boiling parabrombenzylbromide with an alcoholic solution of sodic sulphide; the reaction takes place very easily. The product obtained by distilling off part of the alcohol and precipitating with water was purified by crystallization from alcohol. Dried *in vacuo* it gave the following results on analysis: —

I. 0.1768 g. of substance gave, according to Carius, 0.1780 g. of argentic bromide.

II. 0.1807 g. gave 0.1828 g. of argentic bromide and 0.1057 g. of baric sulphate.

III. 0.2284 g. gave 0.1368 g. of baric sulphate.

	Calculated for $(C_7H_6Br)_2S$.	Found.		
		I.	II.	III.
Bromine	43.01	42.85	43.06	
Sulphur	8.60		8.04	8.23

Properties. — It crystallizes in large thin plates, apparently rhombic crystals, which have a tendency to turn brown in the air; the odor is aromatic, and not especially disagreeable; it melts at 58°–59°; is essentially insoluble in water, soluble with difficulty in cold alcohol, ligroine, or glacial acetic acid, but freely in each of these solvents when hot, and in ether, benzol, or carbonic disulphide.

Parabrombenzylsulphone, $(C_6H_4BrCH_2)_2SO_2$, was made from the sulphide by dissolving it in glacial acetic acid, and adding the calculated amount of chromic anhydride also dissolved in glacial acetic acid. After the action had ceased, the substance was precipitated with water, and purified by crystallization from alcohol. It was analyzed after drying at 100°.

0.1674 g. of substance gave by the method of Carius 0.1556 g. of argentic bromide and 0.0991 g. of baric sulphate.

	Calculated for $(C_7H_6Br)_2SO_2$.	Found.
Bromine	39.60	39.56
Sulphur	7.92	8.13

It crystallizes in white needles, with a slight not unpleasant smell; melts at 189°, and is essentially insoluble in water, soluble only to a slight extent in cold alcohol, benzol, ligroine, and glacial acetic acid, freely soluble in all these solvents when hot, and in ether and carbonic disulphide whether cold or hot.

Parabrombenzylmercaptan, $C_6H_4BrCH_2SH$.

This substance was made by the action of parabrombenzylbromide on an alcoholic solution of potassic sulphydrate. The action took place very easily, and the product fell as an oil on the addition of water to the alcoholic solution. It was purified by distillation with steam, and solidified to a white crystalline mass after standing some time. It had a disagreeable odor, and melted at 25°, but we cannot be perfectly certain that this is the true melting-point, on account of its strong tendency to pass into the disulphide on exposure to the air. The number given above, however, cannot be far from the correct one, as the sample was treated with zinc and sulphuric acid immediately before taking the melting-point. It dissolves easily in all the common solvents with the exception of water and glacial acetic acid. It did not seem worth while to analyze the free mercaptan, as the results obtained from it are almost identical with those from its principal impurity, the disulphide; but instead of this, we determined its nature much more satisfactorily by converting it into the mercaptid, which was then analyzed.

Parabrombenzylmercaptid, $(C_6H_4BrCH_2S)_2Hg$.

This substance was made by adding yellow mercuric oxide to the mercaptan suspended in water; after the action had ceased, the insolu-

ble residue was purified by crystallization from boiling alcohol, and dried at 100°.

0.2623 g. of substance gave on precipitation with sulphuretted hydrogen 0.1016 g. of mercuric sulphide.

	Calculated for $(C_7H_6BrS)_2Hg$.	Found.
Mercury	33.11	33.38

It crystallizes from boiling alcohol as a light white feathery mass with a pearly lustre. It does not melt, but is decomposed and blackened at a high temperature, is essentially insoluble in water, very slightly soluble in cold alcohol, benzol, or glacial acetic acid, freely soluble in hot alcohol (the solution becomes nearly solid on cooling) and benzol, less so in hot glacial acetic acid, but freely in ether and carbonic disulphide.

Parabrombenzyldisulphide, $(C_6H_4BrCH_2)_2S_2$.

This substance was made from the mercaptan by exposure to the air, and also by acting on the parabrombenzylbromide with an alcoholic solution of sodic disulphide; the product precipitated with water was purified by crystallization from alcohol, and dried *in vacuo*.

0.1600 g. of the substance gave by the method of Carius 0.1487 g. of argentic bromide and 0.1838 g. of baric sulphate.

	Calculated for $(C_7H_6Br)_2S_2$.	Found.
Bromine	39.60	39.57
Sulphur	15.84	15.78

It crystallizes in radiating groups of white needles, and has a not unpleasant aromatic smell; melting-point, 87°–88°. It is essentially insoluble in water, slightly soluble in cold alcohol, and almost insoluble in cold glacial acetic acid, but freely soluble in both these solvents when hot, and in ether, benzol, and carbonic disulphide.

The following table gives the formulas and melting-points of the substances described in this paper.

Name.	Formula.
Parabrombenzylsulpho-acid	
Potassium Salt*	$C_6H_4BrCH_2SO_3K$
Calcium Salt	$(C_6H_4BrCH_2SO_3)_2Ca$

* The solution saturated at 18° contains 6.20 per cent of the salt.

Name.	Formula.	Melting-point.
Barium Salt *	$(C_6H_4BrCH_2SO_3)_2BaH_2O$	
Lead Salt †	$(C_6H_4BrCH_2SO_3)_2Pb$	
Chloride	$C_6H_4BrCH_2SO_2Cl$	115°
Parabrombenzylsulphide	$(C_6H_4BrCH_2)_2S$	58°–59°
Parabrombenzylsulphone	$(C_6H_4BrCH_2)_2SO_2$	189°
Parabrombenzylmercaptan	$C_6H_4BrCH_2SH$	25°
Parabrombenzylmercaptid	$(C_6H_4BrCH_2S)_2Hg$	
Parabrombenzyldisulphide	$(C_6H_4BrCH_2)_2S_2$	87°–88°

* The solution saturated at 18° contains 40.50 per cent of the salt.

† The solution saturated at 18° contains 2.00 per cent of the salt.